Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Vibrational Spectra of Small Methylamine Clusters Accessed by an Ab-Initio Anharmonic Approach

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**Parallelization Scheme to Generate Hamiltonian Matrix**

Since we only included semi-diagonal terms (e.g., 3-body interaction terms) in the quartic potential, and we primarily focus on the interaction between stretching and bending modes, we only need to include direct product basis up to 4-body to build the vibrational Hamiltonian with $N$ normal modes. Hence, the dimension of Hamiltonian matrix grows at $O(N^4)$ and the total quantity of matrix elements is proportional to the square of the matrix dimension. With quartic potential, the matrix elements between two harmonic states with different quantum number in more than 3 modes must be zero, thus the Hamiltonian matrix becomes sparser as the matrix dimension increases. Table S2 summarizes the computation time of the Hamiltonian matrix with different sizes (also shown in Figure S4); systems with 24 DOFs needs about two days to build using a single CPU core and the matrix with 36 DOFs takes about 42 days. Therefore, parallelization is necessary to generate the Hamiltonian matrix for large systems.

The calculation of any Hamiltonian matrix elements is independent to each other; hence the parallelization can be achieved by simply assigning the matrix elements to multiple CPU cores. Note that longer time is needed in the evaluation of the matrix elements whose two basis kets are similar; to balance the loading of each CPU cores, we split the Hamiltonian matrix by numbering all matrix elements, then obtained the remainder by dividing the numbers by the total amount of available cores. The matrix element is then assigned to the specific CPU core according to the remainder. Since all neighboring matrix elements are distributed to separate cores, we can thus ensure the similar loading of all cores. Applying this technique, the computation of the whole Hamiltonian matrix of a 36 DOFs system can be finished within 6 hours using 192 CPU cores, as shown in Figure S5.

Figure S4 also shows that the time needed to diagonalize the Hamiltonian matrix grow at roughly square of the matrix dimension, which means parallelized sparse-matrix diagonalization method will be necessary for even larger systems.

**Table S1.** Cartesian coordinates of (MMA)n optimized by MP2/aug-cc-pVDZ.

**MMA**

| | | | |
|---|---|---|---|
| N | -1.764073 | 0.714375 | -0.000295 |
| H | -1.418393 | -0.244641 | -0.033663 |
| H | -1.417023 | 1.164251 | -0.847342 |
| C | -1.233323 | 1.401089 | 1.189572 |
| H | -1.612478 | 2.433586 | 1.203573 |
| H | -1.615138 | 0.898753 | 2.090618 |
| H | -0.130119 | 1.437405 | 1.255693 |

**MMA_2a**

| | | | |
|---|---|---|---|
| N | -2.980786 | 0.090303 | -0.408734 |
| C | -3.442515 | -0.464043 | 0.873658 |
| H | -3.575467 | 0.874343 | -0.676490 |
| H | -2.035656 | 0.469383 | -0.295413 |
| N | 0.161491 | 0.317226 | -0.212864 |
| C | 0.127277 | -1.137888 | 0.034247 |
| H | 0.887950 | 0.752080 | 0.355867 |
| H | 0.422850 | 0.495269 | -1.183012 |
| H | -3.433848 | 0.247798 | 1.720917 |
| H | -2.803105 | -1.318293 | 1.143716 |
| H | -4.468055 | -0.847160 | 0.760124 |
| H | -0.685674 | -1.576330 | -0.562440 |
| H | -0.104241 | -1.310975 | 1.095544 |
| H | 1.066897 | -1.666955 | -0.204500 |

**MMA_2b**

| | | | |
|---|---|---|---|
| N | -2.772298 | 0.082847 | 0.376475 |
| H | -3.105734 | 0.792010 | 1.029506 |
| C | -3.695676 | -0.012428 | -0.764781 |
| H | -1.853372 | 0.396949 | 0.049810 |
| N | 0.296418 | 0.268488 | -0.376439 |
| H | 0.368901 | -0.548614 | -0.983261 |
| C | 0.612603 | -0.114161 | 1.014138 |
| H | 0.987291 | 0.934338 | -0.722324 |
| H | -3.841955 | 0.928986 | -1.327941 |
| H | -4.680430 | -0.355993 | -0.412993 |
| H | -3.316241 | -0.770578 | -1.466629 |
| H | 0.564126 | 0.783692 | 1.647872 |
| H | 1.605405 | -0.578879 | 1.149019 |
| H | -0.157114 | -0.814117 | 1.369191 |

**MMA_3a**

| | | | |
|---|---|---|---|
| N | -0.241209 | -1.868851 | -0.245438 |
| H | -0.142551 | -2.668007 | -0.870834 |

| | | | |
|---|---|---|---|
| H | 0.679597 | -1.421545 | -0.171934 |
| N | -1.256382 | 1.037471 | 0.134503 |
| H | -2.008878 | 1.081076 | 0.821754 |
| H | -1.187235 | 0.055710 | -0.160588 |
| N | 1.800848 | 0.387580 | 0.172453 |
| H | 2.533260 | 0.773119 | 0.767969 |
| H | 0.917169 | 0.822253 | 0.462642 |
| C | -0.643990 | -2.327156 | 1.095872 |
| H | -0.692978 | -1.453632 | 1.764190 |
| H | -1.649723 | -2.772139 | 1.048705 |
| H | 0.039080 | -3.064325 | 1.555726 |
| C | 2.060581 | 0.741236 | -1.234183 |
| H | 3.019197 | 0.304632 | -1.552966 |
| H | 1.270104 | 0.299465 | -1.860753 |
| H | 2.090755 | 1.827258 | -1.440091 |
| C | -1.596031 | 1.882993 | -1.023222 |
| H | -1.662699 | 2.934298 | -0.704564 |
| H | -0.786014 | 1.813058 | -1.764641 |
| H | -2.542477 | 1.615188 | -1.528145 |

**MMA_3b**

| | | | |
|---|---|---|---|
| N | -1.597422 | -0.890983 | 2.475889 |
| H | -2.269576 | -0.955978 | 3.240109 |
| C | -2.312556 | -0.862064 | 1.188241 |
| H | -1.091808 | -0.005963 | 2.604588 |
| N | 1.370646 | -1.690345 | 1.909339 |
| C | 1.420717 | -1.993040 | 0.468453 |
| H | 0.396954 | -1.736365 | 2.233823 |
| H | 1.883884 | -2.403148 | 2.427558 |
| N | 0.597969 | 1.320536 | 2.235563 |
| H | 1.083102 | 1.975088 | 2.848966 |
| C | 0.558199 | 1.861574 | 0.865915 |
| H | 1.145524 | 0.451279 | 2.243079 |
| H | -3.005738 | -0.009741 | 1.063163 |
| H | -2.886863 | -1.792527 | 1.064391 |
| H | -1.575606 | -0.821013 | 0.371674 |
| H | 0.889099 | -1.201299 | -0.081188 |
| H | 0.973203 | -2.963237 | 0.183772 |
| H | 2.466406 | -1.983744 | 0.125862 |
| H | 1.549646 | 2.035772 | 0.408428 |
| H | 0.006130 | 2.813478 | 0.861333 |
| H | 0.006869 | 1.160259 | 0.221110 |

**MMA_4a**

| | | | |
|---|---|---|---|
| N | 0.267386 | -2.076057 | 0.430348 |
| H | 1.011501 | -1.387142 | 0.251153 |
| H | 0.648922 | -2.989033 | 0.183096 |
| N | -2.071172 | -0.266267 | -0.432362 |

| | | | |
|---|---|---|---|
| H | -1.383865 | -1.012052 | -0.254087 |
| H | -2.984507 | -0.645185 | -0.182407 |
| N | -0.266023 | 2.076019 | 0.430617 |
| H | -1.010109 | 1.387304 | 0.250558 |
| H | -0.647260 | 2.989214 | 0.183724 |
| N | 2.072837 | 0.266330 | -0.431487 |
| H | 2.986162 | 0.645279 | -0.181545 |
| H | 1.385533 | 1.012155 | -0.253380 |
| C | -2.052910 | 0.081238 | -1.864141 |
| H | -2.832047 | 0.830342 | -2.073515 |
| H | -1.081781 | 0.540329 | -2.104977 |
| H | -2.206742 | -0.774107 | -2.547349 |
| C | -0.081343 | -2.054941 | 1.861788 |
| H | -0.542413 | -1.084049 | 2.099821 |
| H | -0.829117 | -2.835003 | 2.072455 |
| H | 0.773734 | -2.205434 | 2.546085 |
| C | 2.054653 | -0.081397 | -1.863216 |
| H | 2.833768 | -0.830574 | -2.072419 |
| H | 1.083517 | -0.540480 | -2.104038 |
| H | 2.208577 | 0.773834 | -2.546546 |
| C | 0.081764 | 2.053900 | 1.862275 |
| H | 0.542522 | 1.082776 | 2.099957 |
| H | 0.829527 | 2.833696 | 2.073964 |
| H | -0.773745 | 2.204073 | 2.546103 |

**MMA_4b**

| | | | |
|---|---|---|---|
| N | -2.096316 | 2.551797 | -0.624214 |
| C | -1.023898 | 1.841364 | -1.343365 |
| H | -1.817456 | 2.644653 | 0.360770 |
| H | -2.206493 | 3.493622 | -0.999296 |
| N | -3.885094 | 0.165140 | 0.072675 |
| H | -3.494607 | 0.983040 | -0.414086 |
| C | -4.335440 | 0.611602 | 1.403905 |
| H | -4.683186 | -0.158966 | -0.473262 |
| N | -1.283510 | -1.012487 | 1.175663 |
| H | -0.687820 | -1.584937 | 0.577220 |
| H | -2.129728 | -0.797015 | 0.628853 |
| C | -1.667048 | -1.785462 | 2.370226 |
| N | -0.826480 | 1.913198 | 2.137752 |
| H | -1.125707 | 1.994944 | 3.109760 |
| C | 0.584087 | 2.323204 | 2.022391 |
| H | -0.906766 | 0.917660 | 1.885555 |
| H | -0.058435 | 2.379692 | -1.379836 |
| H | -1.339534 | 1.638600 | -2.378539 |
| H | -0.855551 | 0.874893 | -0.845355 |
| H | -5.118638 | 1.391306 | 1.384181 |
| H | -3.468150 | 1.022735 | 1.942091 |
| H | -4.719368 | -0.247181 | 1.976426 |
| H | -2.293997 | -1.152572 | 3.016966 |
| H | -0.766521 | -2.055426 | 2.942900 |

| | | | |
|---|---|---|---|
| H | -2.230486 | -2.712403 | 2.157027 |
| H | 0.683538 | 3.389642 | 2.276566 |
| H | 0.903421 | 2.199417 | 0.976630 |
| H | 1.283929 | 1.750790 | 2.658966 |

**MMA_4c**

| | | | |
|---|---|---|---|
| N | -2.368711 | 2.834067 | 0.214884 |
| C | -1.754324 | 3.076763 | -1.102044 |
| H | -1.627487 | 2.621084 | 0.897772 |
| H | -2.822883 | 3.687199 | 0.541307 |
| N | -3.535181 | -0.034606 | 0.244536 |
| H | -3.366637 | 0.981263 | 0.263096 |
| H | -4.533176 | -0.166540 | 0.080219 |
| C | -2.767945 | -0.615219 | -0.870854 |
| N | -1.725186 | -0.808514 | 2.637352 |
| C | -1.002866 | -2.003526 | 2.167377 |
| H | -2.478869 | -0.587234 | 1.970956 |
| H | -2.180070 | -1.013427 | 3.527155 |
| N | -0.050441 | 1.697527 | 1.927642 |
| H | 0.532085 | 2.125975 | 2.647013 |
| C | 0.804296 | 1.122936 | 0.874494 |
| H | -0.570535 | 0.932309 | 2.380068 |
| H | -0.991085 | 3.877056 | -1.113779 |
| H | -2.534010 | 3.337217 | -1.834306 |
| H | -1.274098 | 2.148783 | -1.447901 |
| H | -3.012106 | -0.198010 | -1.865396 |
| H | -2.925211 | -1.704162 | -0.907408 |
| H | -1.696061 | -0.443010 | -0.689053 |
| H | -1.639234 | -2.894342 | 2.010482 |
| H | -0.214346 | -2.269360 | 2.888156 |
| H | -0.510266 | -1.769374 | 1.211398 |
| H | 1.365883 | 1.923532 | 0.368990 |
| H | 0.161102 | 0.644657 | 0.120045 |
| H | 1.527612 | 0.365510 | 1.229335 |

**MMA_4d**

| | | | |
|---|---|---|---|
| N | 0.267386 | -2.076057 | 0.430348 |
| H | 1.011501 | -1.387142 | 0.251153 |
| H | 0.648922 | -2.989033 | 0.183096 |
| N | -2.071172 | -0.266267 | -0.432362 |
| H | -1.383865 | -1.012052 | -0.254087 |
| H | -2.984507 | -0.645185 | -0.182407 |
| N | -0.266023 | 2.076019 | 0.430617 |
| H | -1.010109 | 1.387304 | 0.250558 |
| H | -0.647260 | 2.989214 | 0.183724 |
| N | 2.072837 | 0.266330 | -0.431487 |
| H | 2.986162 | 0.645279 | -0.181545 |
| H | 1.385533 | 1.012155 | -0.253380 |

| | | | |
|---|---|---|---|
| C | -2.052910 | 0.081238 | -1.864141 |
| H | -2.832047 | 0.830342 | -2.073515 |
| H | -1.081781 | 0.540329 | -2.104977 |
| H | -2.206742 | -0.774107 | -2.547349 |
| C | -0.081343 | -2.054941 | 1.861788 |
| H | -0.542413 | -1.084049 | 2.099821 |
| H | -0.829117 | -2.835003 | 2.072455 |
| H | 0.773734 | -2.205434 | 2.546085 |
| C | 2.054653 | -0.081397 | -1.863216 |
| H | 2.833768 | -0.830574 | -2.072419 |
| H | 1.083517 | -0.540480 | -2.104038 |
| H | 2.208577 | 0.773834 | -2.546546 |
| C | 0.081764 | 2.053900 | 1.862275 |
| H | 0.542522 | 1.082776 | 2.099957 |
| H | 0.829527 | 2.833696 | 2.073964 |
| H | -0.773745 | 2.204073 | 2.546103 |

**MMA_4e**

| | | | |
|---|---|---|---|
| N | -1.873822 | 2.605110 | -0.326949 |
| H | -1.200027 | 2.983568 | -0.992773 |
| H | -1.360841 | 2.442482 | 0.551061 |
| C | -2.942903 | 3.590668 | -0.091338 |
| N | -3.201207 | -0.192129 | -0.141718 |
| H | -2.698854 | 0.657350 | -0.433824 |
| C | -4.351741 | 0.211919 | 0.686105 |
| H | -3.531549 | -0.648958 | -0.991623 |
| N | -1.651226 | -1.157667 | 2.338638 |
| C | -0.586679 | -2.150417 | 2.112964 |
| H | -2.159072 | -0.996389 | 1.457407 |
| H | -2.330320 | -1.528977 | 3.003095 |
| N | -0.309911 | 1.631958 | 2.141043 |
| H | 0.032493 | 2.087648 | 2.986768 |
| C | 0.828897 | 1.217615 | 1.302170 |
| H | -0.815876 | 0.786861 | 2.439426 |
| H | -2.589716 | 4.576694 | 0.263075 |
| H | -3.633565 | 3.189438 | 0.665406 |
| H | -3.518246 | 3.745595 | -1.017201 |
| H | -5.057705 | 0.902085 | 0.188652 |
| H | -3.973684 | 0.708463 | 1.593429 |
| H | -4.913628 | -0.680415 | 1.003747 |
| H | -0.943745 | -3.136052 | 1.761342 |
| H | -0.016882 | -2.304326 | 3.042415 |
| H | 0.110048 | -1.756668 | 1.357856 |
| H | 1.392973 | 2.105193 | 0.975177 |
| H | 0.437640 | 0.720310 | 0.400899 |
| H | 1.535907 | 0.524783 | 1.794409 |

**Table S2:** The size of Hamiltonian matrices.

| DOFs considered in this work | | | | |
|---|---|---|---|---|
| | MMA | $(MMA)_2$ | $(MMA)_3$ | $(MMA)_4$ |
| NH | 3 | 6 | 9 | 12 |
| CH | 6 | 12 | 18 | 24 |
| NH+CH | 9 | 18 | 27 | 36 |

| Hamiltonian Matrix Size | | | | |
|---|---|---|---|---|
| | MMA | $(MMA)_2$ | $(MMA)_3$ | $(MMA)_4$ |
| NH | $84^2$ | $887^2$ | $4165^2$ | $12888^2$ |
| CH | $887^2$ | $12888^2$ | $64624^2$ | $204155^2$ |
| NH+CH | $4165^2$ | $64624^2$ | $327178^2$ | $1036042^2$ |

| Non-zero Matrix Elements: number (ratio%) | | | | |
|---|---|---|---|---|
| | MMA | $(MMA)_2$ | $(MMA)_3$ | $(MMA)_4$ |
| NH | 1840 (26%) | 110843 (14%) | 1022661 (5.9%) | 3065700 (1.85%) |
| CH | 74509 (9.5%) | 3939492 (2.4%) | 25367476 (0.61%) | 71313611 (0.17%) |
| NH+CH | 523663 (3.0%) | 21747710 (0.52%) | 158007208 (0.15%) | 412163860 (0.038%) |

| Matrix Element Time Cost | | | | |
|---|---|---|---|---|
| | MMA | $(MMA)_2$ | $(MMA)_3$ | $(MMA)_4$ |
| NH | 1 s | 8 s | 110 s | 16 m |
| CH | 8 s | 16 m | 6.9 hr | 42.7 hr |
| NH+CH | 113 s | 5.0 hr | 6.9 day | 42.2 day |

| Diagonalization Time Cost | | | | |
|---|---|---|---|---|
| | MMA | $(MMA)_2$ | $(MMA)_3$ | $(MMA)_4$ |
| NH | 3 s | 3 s | 4 s | 13 s |
| CH | 3 s | 25 s | 8.3 m | 2 hr |
| NH+CH | 3 s | 6 m | 2.56 hr | 40 hr |

**Figure S1:** Calculated vibrational spectra of two $(MMA)_2$ conformers

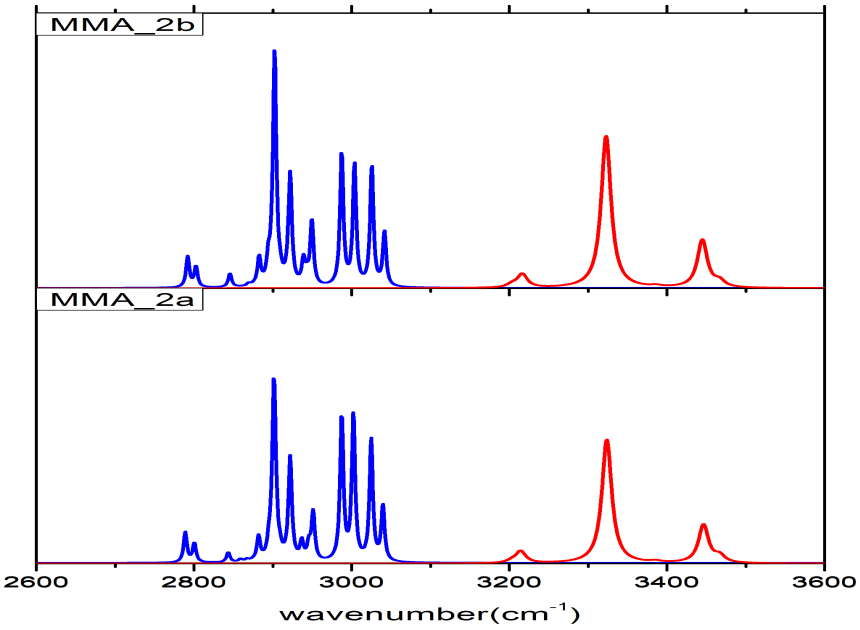

**Figure S2:** Calculated vibrational spectra of two $(MMA)_3$ conformers

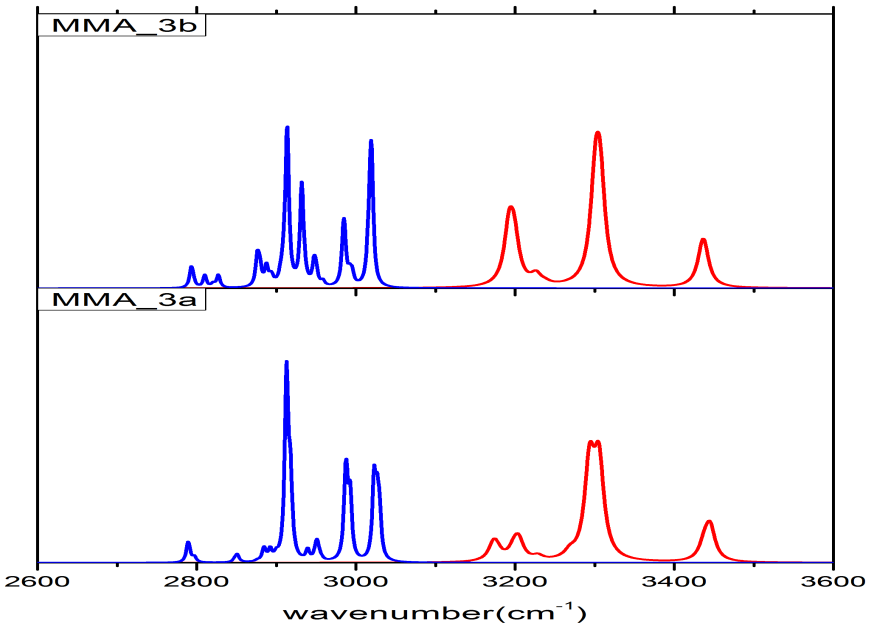

**Figure S3:** Calculated vibrational spectra of all five $(MMA)_4$ conformers

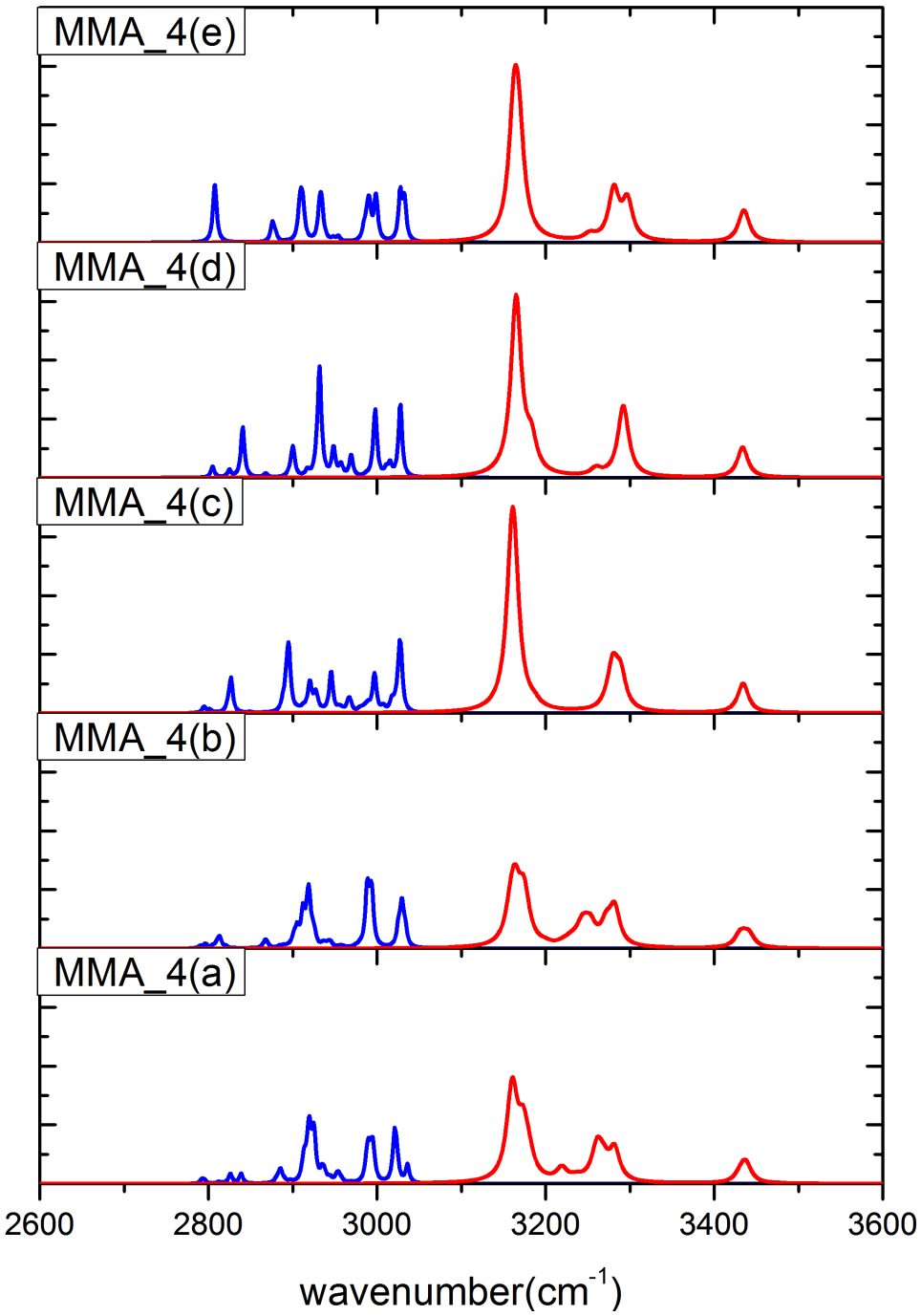

Figure S4: Time-Matrix Size dependence of our Ab-Initio Anharmonic Approach.

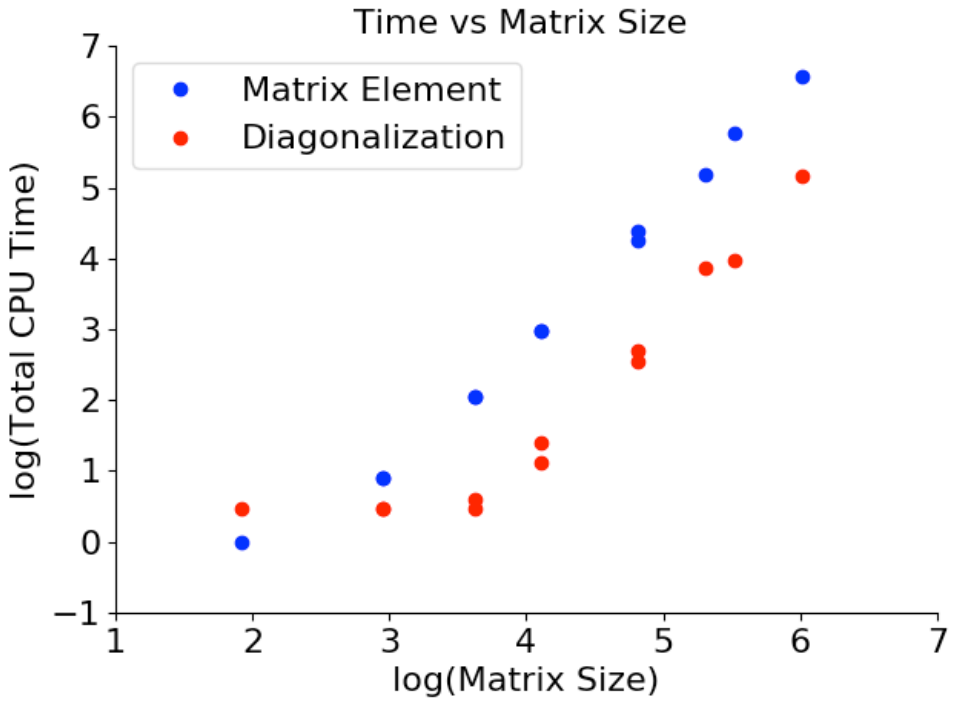

Figure S5: Individual wall time used by 192 cores while generating the Hamiltonian matrix of 36 DOFs system using our parallelization scheme